PATENT SPECIFICATION 945,227

DRAWINGS ATTACHED.

945,227

Date of Application and filing Complete Specification :
Feb. 13, 1962.   *No. 5411/62.*

Application made in United States of America (No. 136,308)
on Sept. 6, 1961.

Complete Specification Published : Dec. 23, 1963.

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Index at Acceptance :—Class C7 A(1, 3, 8A3, 8J, 8K, 8M, 8R, 8U, 8V, 8W, 8Y, 8Z5).
International Classification :—B 23 n, C 22 c.

COMPLETE SPECIFICATION.

Process for Making Hard Surfacing Material.

ERRATA

SPECIFICATION NO. 945,227

Page 1, Heading, Index at Acceptance, *delete* "Class"

Page 1, line 25, *for* "sufaced" *read* "surfaced"

Page 2, line 94, *after* "numeral" *insert* "11"

Page 3, line 56, *for* "long" *read* "along"

Page 5, line 117, *for* "grap" *read* "gray"

Page 6, line 87, *for* "difference" *read* "differences"

Page 7, line 25, *for* "specimens" *read* "specimen"

Page 7, line 68, *for* "alley" *read* "alloy"

Page 7, line 69, *after* "cemented" *insert* "carbide"

Page 8, line 6, *for* "Run" *read* "Runs"

Page 8, line 34, *for* "Run" *read* "Runs"

Page 8, line 66, *for* "mould" *read* "mold"

Page 9, line 74, *for* "0.0015" *read* "0.015"

Page 8, line 119, *for* "infiltrated" *read* "infiltration"

THE PATENT OFFICE,
31st March, 1964

D 3834/1(6)/R.109 200 3/64 PL

terials produced in this manner are normally
superior to those produced by other pro-
cesses but are not entirely satisfactory for
40 all purposes. Experience has shown that
cemented carbide particles bonded to oil
field drill bits and similar tools with a matrix

[*Price 4s. 6d.*]

work have shown that this halo is much
softer and considerably weaker than the un- 80
altered center or "core" of the particle and
that this change in particle structure is
largely responsible for the poor performance
obtained with hard surfacing materials pre-

Price 75p

pared in the manner described earlier. Because of the apparent relationship between the formation of a cobalt-matrix alloy and the bonding of cemented carbide particles in place within the matrix, degradation of the particles has been considered unavoidable.

It is therefore the object of the present invention to provide a process for the production of improved hard surfacing materials which are considerably stronger and more resistant to abrasion and erosion than materials available heretofore.

In accordance with the present invention, it has now been found that improved hard surfacing materials containing cemented hard metal carbide particles supported in a matrix of softer, more ductile metal can be prepared by infiltrating the matrix metal into the interstices between the carbide particles under carefully controlled conditions. Studies and laboratory work have demonstrated that metallurgical bonding of cemented hard metal carbide particles within a matrix of softer metal having the ability to wet the carbide does not depend upon the replacement of large quantities of the cobalt (or other cementing metal) by the matrix metal and that the infiltration process used to produce hard surfacing materials containing such particles can therefore be controlled to minimize alloying between the matrix metal and cobalt without sacrificing the strength contributed by a metallurgical bond. Moreover, it has been found that proper control of the infiltration conditions results in a hardening rather than a softening of the carbide particles. This makes possible the production of hard surfacing materials containing cemented carbide particles which have exceptional strength and hardness. Such materials have considerably greater resistance to abrasion and erosion than hard surfacing materials available in the past.

In carrying out the process of the invention, a mass comprising discrete particles of cemented hard metal carbide and a quantity of matrix metal sufficient to fill the interstices between the particles are separately heated to the required infiltration temperature in an electric furnace. After the requisite temperature has been reached, the molten matrix metal is poured from the crucible or other vessel in which it was heated into the mold containing the particles. The mold is then held at the infiltration temperature long enough to cause reaction of the matrix metal with the surfaces of the cemented carbide particles, but insufficient to produce significant degradation of the particles. At the end of this reaction period, the mold is removed from the furnace and rapidly cooled to a temperature below the matrix melting point. Experimental work has shown that thus preventing premature contact between the molten matrix

and carbide particles, limiting the furnacing time, and quickly cooling the mold following infiltration results in hardening of the particles and permits the formation of a strong metallurgical bond without serious degradation of the particle structure.

Reference will now be made to the accompanying drawing, in which:—

Figure 1 represents schematically a vertical section through an electric furnace containing a mold and crucible suitable for use in the preparation of the hard surfacing material of the invention;

Figure 2 is a reproduction of a photomicrograph showing a cemented tungsten carbide particle partially destroyed by the formation of an alloy between the cobalt in the particle and the surrounding matrix metal; and

Figure 3 is a reproduction of a photomicrograph showing a cemented tungsten carbide particle which has been metallurgically bonded in place within a matrix of softer metal without the formation of a cobalt-matrix alloy in significant quantities.

The process of the invention may be carried out in an electric furnace of either the resistance or the induction type. Reference numeral in Figure 1 of the drawing designates a bottom-loading electric furnace of the resistance type lined with refractory 12 and provided with a door 13 which is opened and closed by raising and lowering it. A furnace of this type is generally preferred for purposes of the invention because of the relatively small temperature drop which takes place when the furnace is opened. Reference numeral 14 designates the mold employed to hold the cemented carbide particles to be infiltrated with the molten matrix metal; while reference numeral 15 indicates the crucible in which the matrix metal is melted.

The refractory mold employed in preparing the hard surfacing material of the invention will normally include a lower mold section 14a provided with threads 14b for attaching an upper section or cover 14c. The lower section contains a recess within which the hard metal carbide particles and the tool or part to which they are to be bonded may be placed. The shape of this recess will depend upon the desired configuration of the finished tool. It should be designed to accommodate the tool so that the surfaces to which the carbide particles are to be bonded are readily accessible. Sufficient space must be left adjacent the surfaces to permit addition of the required carbide particles. It is generally preferred to machine a large recess in the lower section of the mold and then insert spacers 14d of refractory material to obtain a smaller recess of the desired shape. Sand, strips of clay, or similar material 14e may be placed be-

copper-cobalt-tin alloys, copper-nickel-iron-tin alloys and copper-nickel-manganese alloys. Such alloys may contain minor amounts of other elements including zinc, manganese, molybdenum, iron, silicon, beryllium, bismuth, boron, cadmium, cobalt and phosphorus. A number of other commercially available alloys which melt within the above specified temperature range and will wet the carbide and steel may be utilized for purposes of the invention and will be familiar to those skilled in the art. It will be understood, of course, that every alloy has slightly different properties and that certain alloys are therefore more effective for purposes of the invention than are others. The use of copper-nickel-tin or copper-nickel-manganese alloys is preferred because of their excellent wetting characteristics and high strength. A small amount of borax or other flux may be added to the matrix metal pellets in crucible 15 in order to aid in the control of oxide formation at elevated temperatures.

It is preferred that the assembled mold 14 containing the tool 16, the carbide particles 17, and the carbide powder be preheated at a temperature between 300° and 600° F. for an hour or longer in order to eliminate gases from the mold which might otherwise cause oxidation at the infiltration temperature. Following this preheating step, the mold and the crucible 15 containing the matrix metal are placed in an electric furnace and heated to a temperature between 1750° F. and 2500° F. The temperature employed should not greatly exceed that required for rapid infiltration of the matrix metal into the carbide particles and powder. The composition of the matrix metal and the powder in the mold will govern the infiltration temperature. Copper-nickel alloys will readily infiltrate at temperatures between 2000° F. and 2250° F.; whereas slightly higher temperatures are required for the infiltration of iron-nickel-carbon alloys and the like. The use of powdered nickel in the mold promotes wetting of the carbide powder and generally permits the use of a slightly lower infiltration temperature than might otherwise be necessary. The precise temperature required for a particular matrix alloy and powder can readily be determined by preparing small specimen molds, filling them with cemented carbide particles and powder, pouring the molten matrix metal into them at various temperatures, and later examining the specimens to determine whether infiltration took place.

After the furnace has returned to temperature following the insertion of mold 14 and crucible 15, the mold and crucible are heated for a period of from about 30 minutes to an hour or more in order to melt the matrix metal and bring the contents of the mold up to the infiltration temperature. The time required to reach this temperature will depend upon the type of furnace utilized and upon the size and heat transfer characteristics of the mold. Heating of the cemented carbide particles in the absence of the matrix metal prevents degradation of the particles before the temperature required for complete infiltration is reached. The mold contents can be held at elevated temperatures for long periods prior to infiltration without adverse effects. After sufficient time for the particles to have reached the infiltration temperature has elapsed, the furnace door 13 is opened. The crucible 15 is quickly lifted with a pair of long-handled tongs or a similar tool and the molten matrix metal is poured into the mold. This step should be carried out as rapidly as possible in order to minimize cooling of the mold and furnace while the door is open. The door is then closed and heating is continued for a period of from three minutes to six minutes. During this period, the molten matrix metal flows into the interstices between the carbide particles, the mold and the tool to be hard surfaced. Reaction of the matrix with the carbide at the surfaces of the particles takes place. Some diffusion and alloying of the matrix metal with the cobalt at the surface of the particles will also occur but the extent to which this takes place is limited. Studies have shown that much of the alloying and resultant carbide degradation which occurs in the conventional infiltration process occurs before the final temperature required for complete infiltration is reached. Separate heating of the particles and matrix metal to the infiltration temperature avoids this.

Following the three to six minutes infiltration period, the mold 14 is taken out of the furnace and quickly cooled to a temperature between 1500° F. and 1600° F. within a period of from one to five minutes. The method utilized to cool the mold will depend primarily upon the mold size. In the case of relatively large molds, those a foot or more in diameter for example, a water spray should be used to assure cooling at a sufficiently rapid rate. With smaller molds, an air blast will usually be adequate. An optical pyrometer may be used to check mold temperatures if desired. Rapid cooling below about 1500° F. should be avoided because such cooling may have an adverse effect upon the grain structure of the steel in the tool. The mold is therefore allowed to cool slowly from 1500° F. to 1600° F. down to room temperature in still air. This two stage cooling cycle assures prompt arrest of the cobalt-matrix interaction responsible for halo formation and yet permits the formation of a strong metallurgical bond between the cemented carbide particles, the matrix

hence it can be seen that at least 50% of the original particle was altered in structure by the reaction responsible for formation of the halo.

Figure 3 of the drawing is a reproduction of a photomicrograph showing a cemented tungsten carbide particle in the material prepared by heating the particles and matrix alloy separately, pouring the molten alloy into the mold, and thereafter quickly cooling the mold to a temperature below the matrix melting point. The photomicrographs represented in Figures 2 and 3 were both taken at 60 power magnification. It can be seen that the appearance of the particle shown in Figure 3 is quite different from that of the particle in Figure 2. The light center section representing essentially unaltered tungsten carbide is only slightly smaller than the original particle. A thin bed of dark material caused by reaction between the carbide, cobalt and matrix surrounds the particle and bonds it in place. The matrix metal containing partially dissolved carbide powder can be seen at the edges of the photomicrograph. These photomicrographs demonstrate that the process of the invention results in significantly less alteration of the cemented carbide than does the earlier process and that the final product is structurally different from that obtained in the conventional process.

Following the test described above, microhardness measurements were made to determine the effect of carbide-matrix interaction on the properties of the cemented carbide. The measurements were carried out with a Vickers microhardness tester. Hardness determinations were made at intervals across a series of cemented tungsten carbide particles similar to that shown in Figure 2 of the drawing. In every case it was found that the halo section at the periphery of the cemented carbide particle was significantly softer than the core of the particle. The results of a typical test are shown in Table I below.

TABLE I.
DIAMOND PYRAMID HARDNESS MEASUREMENTS ACROSS A CEMENTED TUNGSTEN CARBIDE PARTICLE.

Reading No.	Location on Particle	Diamond Pyramid Hardness
1	Near edge	920
2		885
3		840
4		850
5		785
6		860
7		1550
8	Center	1550
9		1640

Reading No.	Location on Particle	Diamond Pyramid Hardness
10	Center	1580
11		1640
12		1550
13		960
14		1050
15		1065
16	Near edge	1150

The values in the above table, obtained at intervals of 0.1 millimeter across the particle surface under a 200 gram load, clearly show the effect of halo formation upon the properties of the cemented tungsten carbide. Near the center of the particle, hardness values between 1550 and 1640 were obtained. These correspond to the initial hardness and indicate that the carbide in this central region was not degraded. Near the edges, however, the hardness values dropped sharply. The lower values obtained show that there was a significant change in carbide structure near the edges of the particle. The boundaries of the halo are clearly delineated by the difference between readings 6 and 7 and between readings 12 and 13. It can be seen that the halo was about six-tenths of a millimeter wide on one edge, that the core had about the same width, and that the halo width on the other edge was about four-tenths of a millimeter. The data thus show that a substantial portion of the original carbide was rendered much softer as a result of the halo formation. These soft portions are much less resistant to abrasion and erosion than the original carbide. Microhardness tests similar to those described above were carried out with a Knoop microhardness tester on a cemented carbide particle bonded in place by the process of the invention. The particle used was similar to that shown in Figure 3 of the drawing. The data obtained are set forth in the following table.

TABLE II.
KNOOP HARDNESS MEASUREMENTS ACROSS A CEMENTED TUNGSTEN CARBIDE PARTICLE.

Reading No.	Location on Particle	Knoop Hardness
1	Near edge	1257
2		1332
3		1312
4	Near center	1342
5		1257
6		1244
7		1257
8	Near edge	1222
9		1124

absence of both powder and alloy. No halo was formed. Similar results were obtained in Run 2 where the particles were heated in the presence of a mixture of powdered carbide and nickel without the matrix alloy. In Run 3 through 6, however, the matrix alloy was present and halo formation occurred. It can be seen that the halo increased with increasing exposure of the particles to the alloy at elevated temperatures. The sixty minute exposure period in Run 6 approximates the total exposure time when a large mold containing a steel tool, cemented carbide particles, powder and matrix is heated for a long period or is removed from the furnace after a short infiltration period and allowed to cool in still air. If excessive halo formation is to be avoided, the infiltration period and the cooling rate must be controlled.

Run 7 in Table III was carried out with cast tungsten carbide particles containing only a trace of cobalt. It will be noted that no halo formation occurred. This indicates that it is the cobalt contained in the pores of the sintered carbide structure which is responsible for halo formation and not the tungsten carbide itself. The cast tungsten carbide particles were securely held in place by a metallurgical bond, showing that severe halo formation is not essential to the metallurgical bonding of the carbide particles in the matrix.

Run 8 through 14 in Table III were carried out with two different types of cemented tungsten carbide, three different powder compositions and two different matrix alloys of widely varying properties. In each case a metallurgical bond between the carbide particles and the matrix was formed. The effect of total contact time between the particles and the molten alloy on halo formation is apparent.

To further demonstrate the process of the invention, two sets of steel oil field drag bit blades were hard surfaced. Both sets of blades were produced by infiltrating angular cemented tungsten carbide particles and a minus 170 mesh mixture of 83 weight per cent powdered tungsten carbide and 17 weight per cent nickel with an alloy containing about 35 per cent copper, about 55 per cent nickel and about 10 per cent tin at 2250° F. In one case carbide particles and powder in contact with the steel blades were infiltrated with the matrix alloy in the conventional manner, the mold used was held at the infiltration temperature for approximately 20 minutes, and the blades were then allowed to air cool to room temperature. The second set of blades was prepared by heating the powder and carbide particles in contact with the steel blades in a carbon mold, separately melting the matrix alloy in a crucible, pouring the molten alloy

into the mould, holding the mold to the infiltration temperature of 2250° F. for 4 minutes, water cooling the molds to about 1600° F., and thereafter allowing the blades to cool to room temperature under atmospheric conditions. Metallographic examination showed that the carbide particles in the blades prepared in the conventional manner had halos of about 0.0015 inch and that about 50 to 75 per cent of the total carbide particle volume in the blades had been degraded by halo formation during fabrication of the blades. The carbide particles in the blades prepared in accordance with the invention, on the other hand, had halos of only about 0.002 inch and hence only about 5 per cent of the total particle volume was adversely affected by halo formation.
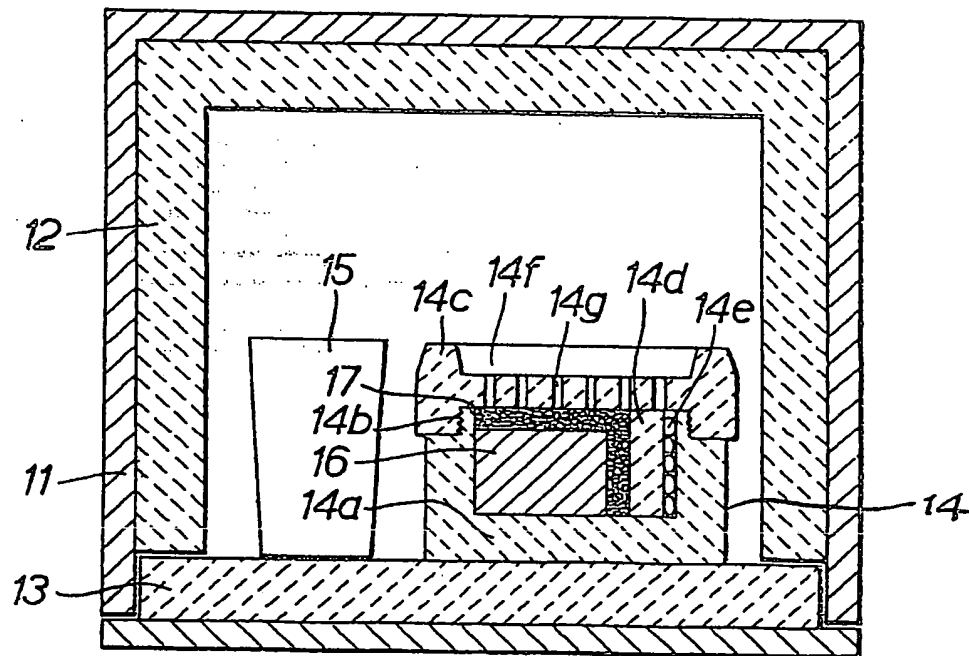
Subsequent drilling tests with bits fitted with the blades prepared as described above were carried out under controlled conditions in a formation of known stratigraphy. The results of these tests demonstrate the superior properties of the blades prepared by the process of the invention. It was found that the blades hard surfaced by separately heating the carbide particles and alloy and later cooling the mold rapidly to a temperature below the alloy melting point drilled 10,250 feet for each inch of blade wear; while the other set drilled 4,556 feet per inch of blade wear. This marked difference in wear rate confirms the effect of halo formation upon the resistance of hard metal carbides to wear and abrasion and demonstrates that hard surfacing materials prepared in accordance with the invention are superior to those prepared in the conventional manner.

WHAT WE CLAIM IS:—

1. A process for the manufacture of a hard surfacing material which comprises heating a mass comprising discrete particles of cemented hard metal carbide to a temperature between 1750° F. and 2500° F.; separately heating to said temperature a metallic composition having the ability in the molten state to wet the cemented carbide particles, sufficient in quantity to fill the interstices between the particles in the mass and having a melting point below said temperature; infiltrating the matrix composition into the interstices between the cemented carbide particles and maintaining the infiltrated mass at the infiltrated temperature for a period sufficient to cause reaction of the matrix composition with the surfaces of the cemented carbide particles, but insufficient to produce a significant degradation of said particles; and thereafter rapidly cooling the infiltrated mass to a temperature below the melting point of the matrix composition.

2. A process according to Claim 1 wherein the cemented carbide particles are

FIG.1.

FIG.2.

FIG.3.

FIG.1.